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Features of the Diels-Alder reaction between 9,10-diphenylanthracene and 4-phenyl-1,2,4-triazoline-3,5-dione

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Abstract

© 2014 Pleiades Publishing, Ltd. The Diels-Alder reaction between substituted anthracenes 1a-1j and 4-phenyl-1,2,4-triazoline-3,5 (2) is studied. In all cases except one, the reaction proceeds on the most active 9,10-atoms of substituted anthracenes. The orthogonality of the two phenyl groups at the 9,10-position of diene 1a is found to shield 9,10-reactive centers. No dienophiles with C=C bonds are shown to participate in the Diels-Alder reaction with 1a; however, the reaction 1a + 2 proceeds with the very active dienophile 2,4-phenyl-1,2,4-triazoline-3,5-dione. It is shown that attachment occurs on the less active but sterically accessible 1,4-reactive center of diene 1a. The structure of adduct 3a is proved by 1H and 13C NMR spectroscopy and X-ray diffraction analysis. The following parameters are obtained for reaction 1a + 2 ⇄ 3a in toluene at 25°C: Keq = 2120 M-1, ΔHf ≠ = 58.6 kJ/mol, ΔSf ≠ = -97 J/(mol K), ΔVf ≠ = -17.2 cm3/mol, ΔHb ≠ = 108.8 kJ/mol, ΔSb ≠ = 7.3 J/(mol K), ΔVb ≠ = -0.8 cm3/mol, ΔHr-n = -50.2 kJ/mol, ΔSr-n = -104.3 J/(mol K), ΔVr-n = -15.6 cm3/mol. It is concluded that the values of equilibrium constants of the reactions 1a-1j + 2 ⇄ 3a-3j vary within 4 × 101-1011 M-1.

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Keywords

4-phenyl-1,2,4-triazoline-3,5-dione, 9,10-diphenylanthracene, Diels-Alder reaction, high pressure, regioselectivity